THE EFFECT OF ORGANIC MATTER ON THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE

A THESIS

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BY

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ACKNOWLEDGMENT

The writer is indebted to Professor John Laurence Daniel whose unselfish labor in connection with suggestions and criticisms of this investigation has contributed much toward the attainment of the results which we hope are of a high degree of accuracy.

The presence of organic matter in the precipitation of phosphorus as ammonium phosphomolybdate has attracted the attention of analytical chemists since the method was first proposed by Sonnenschein (1). Unfortunately, previous investigators (2) have differed considerably as to the effect of organic matter on the reaction. Analysts are still in doubt concerning the accuracy of their work when phosphorus is determined in the presence of organic substances. A knowledge, therefore, of the true effect of organic matter on the reaction can not be over-emphasized. This knowledge may eliminate many of the inconsistent results of phosphorus analyses (3) made by analytical chemists of to-day.

Hundeshagen (4) was one of the first to point out that the presence of polybasic organic acids, such as oxalic and tartaric, prevent entirely the formation of the canary yellow precipitate. He says, "The re-union of the elements of the phosphomolybdic acids is prevented since additional nitric acid added to the solution neither gives a precipitate nor takes on a yellow color." Fresenius (5), also, says, "Certain organic substances, such as tartaric acid and reducing substances, have a disturbing effect on the reaction." Analytical procedures found in several quantitative texts (6) recommend the destruction of all organic matter, present in the sample, before phosphorus is determined as ammonium phosphomolybdate.

On the other hand, Lord and Demorest (7) seem to attribute the bad results obtained in the analysis of phosphorus (most clearly brought out in steel analysis), not to the presence of organic matter but to the fact that all phosphorus is probably not converted into the phosphate ion. They do acknowledge, however, that solutions of organic acids, such as tartaric and oxalic, dissolve the ammonium phosphomolybdate precipitate to some extent. Lundell and Hoffman (8), of the Bureau of Standards, state that they have not found moderate amounts (0.1 to 0.3 g.) of certain organic compounds, such as citric and tartaric acids, to be objectionable in the determination of phosphorus in steel. Furthermore, the statement of Hundeshagen is emphatically contradicted by G. Maderna (9) who says that succinic, malonic, d-tartaric, oxalic, acetic, citric, benzoic, salicylic, and phthalic acids do not prevent the precipitation of ammonium phosphomolybdate if sufficient nitric acid is present.

In some unpublished work recently carried out by former students at this institution (10), the results obtained by them indicate that all organic matter, used in the study, has a disturbing effect on the reaction. Furthermore, their data indicates a possibility that the degree of disturbance of the reaction may bear a direct quantitative relation to the length of

the chain, or the number of hydroxyl or carboxyl groups, present in the organic compound.

As previously shown above, a critical survey of all literature reveals only conflicting information. Our quantitative texts are not very concordant in their recommendation for removal of all organic matter before phosphorus is estimated quantitatively. Qualitative texts (11) have not mentioned that certain organic substances, such as oxalic and tartaric acids, prevent the formation of the canary yellow precipitate and, consequently, destroy the results of the most common method for the detection of phosphorus.

Additional investigation for the purpose of determining the true effect of organic substances on the reaction is of particular interest to the analysts. For some time, many chemists have looked forward to the time when there will be no doubt concerning the effect of organic matter on the formation and precipitation of ammonium phosphomolybdate. With this idea in mind, a study has been made and the results of the investigation are given below.

The official method (12), with a few modifications to suit the conditions present (13), has been used to carry out the study. The greatest of care has been exercised in every determination. A standard method has been used in all determinations of phosphorus.

Moreover, control samples have been run to eliminate the possible errors in solutions.

SOLUTIONS

Molybdate Solution:

100 grams of 85% Molybdic Acid, C.P., were dissolved in a solution containing 144 cc. of ammonium hydroxide (Sp. G. 0.90) and 270 cc. of distilled water. This solution was slowly poured, with constant stirring, into another solution prepared by mixing 570 cc. of Nitric Acid (Sp. G. 1.42) with 1150 cc. of distilled water. This mixture was kept at least 24 hours before use.

Phosphate Solution:

The phosphate solution was prepared by dissolving approximately 1.3 gram of $Na_2HPO_4 \cdot 12H_2O$ in one liter of distilled water.

Organic Compounds:

Organic liquids were added directly, to the sample containing the phosphate, by means of a pipette. The organic solids were weighed directly into the flask containing the sample.

Potassium Nitrate Solution:

A 1% solution of Potassium Nitrate was prepared by dissolving 10 grams of the salt in a liter of solution.

Sodium Hydroxide:

Approximately 4.5 grams of sodium hydroxide was dissolved in about one liter of distilled water and a small quantity of barium hydroxide was added to remove any carbonates from the solution. The barium carbonate was filtered off and the solution diluted to sufficient volume to give a 0.1 normal solution. The base was standardized against 0.1 normal hydrochloric acid using phenolphthalein as an indicator.

Hydrochloric Acid:

Concentrated hydrochloric acid was diluted to approximately 0.1 normal solution. The dilute acid was standardized against pure sodium carbonate using methyl orange as an indicator.

Sodium Carbonate:

The sodium carbonate used in the standardization of the hydrochloric acid was prepared by re-crystallizing chemically pure carbonate twice and then heating it in a watchglass for two hours at 270° C.

Indicator:

The methyl orange and phenolphthalein indicators were prepared in accordance with the recommendation found in Mahin's "Quantitative Analysis."

PROCEDURE

25 cc. of the phosphate solution were pipetted into a 500 cc. erlenmeyer flask. Eight grams of ammonium nitrate dissolved in sufficient distilled water to make 50 cc. of solution were added to the flask. Varying amounts of organic matter were added to several flasks containing the above solution. 50 cc. of freshly filtered acid molybdate solution and sufficient distilled water were added to bring the total volume of the sample to exactly 150 cc. The flask containing the sample was shaken in a mechanical shaker, at room temperature, for exactly 30 minutes. The liquid remaining in the flask after precipitation was decanted immediately through a quantitative filter paper. The precipitate remaining in the flask was washed five times by decantation with exactly 15 cc. portions of the 1% potassium nitrate solution. The precipitate was transferred then to the filter paper and again washed five times with exactly 15 cc. portions of the nitrate solution. The tenth wash water filtrate was tested with blue litmus paper to insure the complete removal of all nitric acid. The filter paper containing the yellow precipitate was transferred to the flask which originally contained the precipitate. 50 cc. of freshly boiled, but cool, distilled water were added.

More than enough sodium hydroxide solution to dis-

solve all the yellow precipitate was run into the flask. After allowing about five minutes for all the precipitate to dissolve, the excess base was titrated with 0.1 N hydrochloric acid using phenolphthalein as an indicator.

The reaction expressing the formation of the yellow precipitate is:

$$H_3PO_4+12(NH_4)_2MoO_4+23HNO_3=(NH_4)_3PO_4\cdot 12MoO_3\cdot 2HNO_3\cdot H_2O + 21NH_4NO_3+11H_2O$$

The action of the nitrate wash is, perhaps, expressed by the equation:

$$(NH_4)_3PO_4\cdot 12MoO_3\cdot 2HNO_3\cdot H_2O+KNO_3 \text{ wash } H_2O=(NH_4)_3PO_4\cdot 12MoO_3 +2HNO_3+KNO_3 \text{ wash } H_2O$$

When the yellow precipitate dissolves in sodium hydroxide the following reaction takes place:

$$2\left[(NH_4)_3PO_4\cdot 12MoO_3\right]+46NaOH=2(NH_4)_2HPO_4+(NH_4)_2MoO_4+ 23Na_2MoO_4+22H_2O$$

1 cc. of 0.1 N sodium hydroxide reacts with ammonium phosphomolybdate containing 0.000309 grams of P_2O_5.

The experimental data are expressed in terms of the number of mols of P_2O_5, present in the ammonium phosphomolybdate, which were held in solution by a certain number of mols of organic matter. The data obtained in this investigation are as follows:

ETHYL ALCOHOL, C_2H_5OH

Sample No.	Mols Added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.597	-0.84*
2	0.597	-1.68
3	0.685	11.89
4	0.685	11.89
5	0.771	39.77
6	0.805	48.44
7	0.805	48.44

The concentration of P_2O_5 in sample is 48.44×10^{-6} mols.

All precipitates were colored yellow. The solutions of samples Nos. 1 and 2 were colorless after precipitation. The other samples contained yellow solutions which indicated that precipitation was not complete. By diluting the volume of the yellow colored filtrates a small yellow precipitate is thrown down immediately. Also, if several grams of ammonium nitrate are added to a yellow solution a sticky yellow precipitate forms but the solution does not become colorless.

Several runs were made using a more concentrated solution of phosphate. The results were similar to those given above. However, when the concentration of the phosphate increases the number of mols of ethyl alcohol required to prevent precipitation also increases.

*Note: The negative sign frequently found in the tabu-

lated data given in this paper indicates that an excessive amount of sodium hydroxide solution was required to dissolve the yellow precipitate. That is, more base was used than should have been used to dissolve the yellow ammonium phosphomolybdate if precipitation had been carried out in the absence of organic matter.

N-PROPYL ALCOHOL, $CH_3 \cdot CH_2 \cdot CH_2OH$

Sample No.	Mols Added	Mols $P_2O_5 x10^{-6}$ held in solution
1	0.134	-0.91
2	0.201	-3.87
3	0.201	-2.67
4	0.268	-2.04
5	0.268	-2.60
6	0.335	3.79
7	0.335	9.65
8	0.402	48.44
9	0.402	48.44

The concentration of P_2O_5 in sample is $48.44x10^{-6}$ mols.

Samples containing 0.5 to 1 mol of alcohol were run but the results of analyses are similar to samples 8 and 9. On the addition of 0.335 mols or more of alcohol, precipitation was not complete and even after filtration the filtrates were colored yellow. As in the case with ethyl alcohol, the yellow filtrates when diluted gave a small yellow precipitate. Increased precipitation from the yellow solutions was not obtained when additional acid molybdate solution was added. The presence of 0.402 mols of alcohol completely prevents the precipitation of ammonium phosphomolybdate.

An additional run was made with entirely new solutions to check the results of the former run given above.

Sample No.	Mols Added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.134	-0.35
2	0.134	-0.42
3	0.201	-0.98
4	0.201	-0.98
5	0.268	-0.92
6	0.268	-0.98
7	0.335	6.40
8	0.335	10.20
9	0.402	46.00
10	0.402	46.00

P_2O_5 in sample equals 46.00×10^{-6} mols.

The results obtained from this run are very similar to the results given in the first run. The duplicate samples of the latter run, however, are in better agreement than those of the first run. The explanation for the better agreement is not known.

It will be observed that the results of samples Nos. 6 and 7 of the first run and samples Nos. 7 and 8 of the last run are not in close agreement. It is not believed that this difference is caused by error in experimental work. The precipitates of all four samples were apparently more soluble than an ordinary yellow precipitate in wash water. The filtrates of these samples were colored yellow.

N-BUTYL ALCOHOL, $CH_3 \cdot (CH_2)_2 \cdot CH_2OH$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.055	-1.48
2	0.082	-3.68
3	0.082	-4.36
4	0.109	-0.70
5	0.109	-2.25
6	0.137	11.12
7	0.137	10.84
8	0.164	48.44
9	0.164	48.44

Mols of P_2O_5 in sample equals 48.44×10^{-6}

The precipitates from the first five samples were yellow in color. The remaining four samples failed to give the ordinary canary yellow precipitate. Yellow oily droplets were formed in sample No. 6. Sample No. 7 gave red oily droplets even though the concentration of organic matter is the same as it is in sample No. 6. In the other two samples, Nos. 8 and 9, a yellowish brown oil-like substance formed on the surface of the liquid. On dissolving precipitates from samples Nos. 6 and 7 in excess base and titrating the excess base with acid the color of the remaining solutions were quite different. On titration, sample No. 6 gave a colorless

solution. Sample No. 7 gave a dark brown solution and the end-point was difficult to determine with phenolphthalein as an indicator. The precipitates of samples 8 and 9 completely dissolved in the wash water and no determination of the phosphorus was attempted.

Sec-BUTYL ALCOHOL, $CH_3 \cdot CH_2 \cdot CHOH \cdot CH_3$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.055	0.07
2	0.055	0.21
3	0.111	0.07
4	0.166	1.20
5	0.166	1.06
6	0.193	18.73
7	0.193	19.08
8	0.221	31.96
9	0.221	33.65
10	0.249	34.43
11	0.249	30.91
12	0.276	33.58
13	0.276	38.44

The concentration of P_2O_5 in sample is 48.44×10^{-6}

Samples Nos. 1, 2, and 3 gave yellow precipitates. Greenish yellow precipitates were precipitated in samples 4 and 5. Beginning with sample No. 6 and continuing through No. 13 a brownish yellow jelly-like substance settled to the bottom of the flasks. The solutions were colorless as though all phosphorus had been precipitated as yellow ammonium phosphomolybdate. On washing the precipitates of samples Nos. 6 to 13 the jelly changed to a yellow colored precipitate and the

wash water added to the filtrate caused more yellow precipitate to form. The yellow precipitates formed from the jelly and from the filtrate were not canary yellow ones. They were of a much deeper color.

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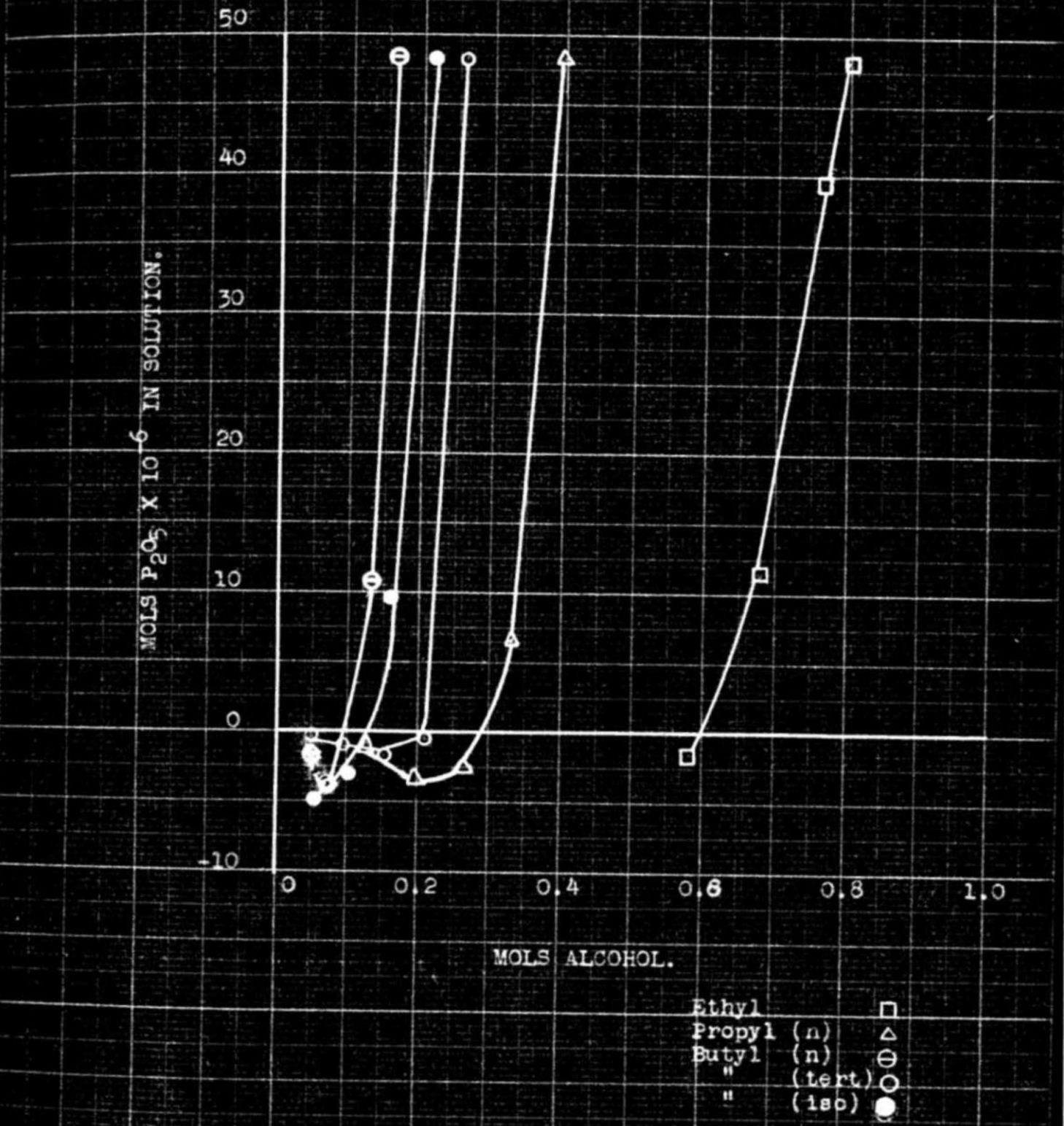
ISO-BUTYL ALCOHOL, $(CH_3)_2CH \cdot CH_2OH$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.054	-6.12
2	0.054	-3.59
3	0.109	-3.31
4	0.109	-2.67
5	0.163	7.95
6	0.163	11.54
7	0.218	48.44
8	0.218	48.44

48.44×10^{-6} mols of P_2O_5 are present in each sample.

Ordinary yellow precipitates were formed in samples 1, 2, 3, and 4. However, the remaining four samples underwent peculiar reactions. Instead of a yellow precipitate, brown oily droplets appeared in the bottom of both samples 5 and 6. There were no precipitates formed in flasks 7 and 8. A greenish yellow oil, however, appeared on the surface of the solutions. The brown oily droplets and the greenish yellow oil were filtered from the solutions. On washing the precipitates with wash water further changes took place. The greenish yellow oil dissolved in the water. On diluting the filtrate, a yellow precipitate formed which had a tendency to stick to glass. Instead of the brown oily droplets dissolving in the wash water, a yellow

sticky precipitate formed on the filter paper. The filtrates from samples 5 and 6, also, yielded a yellow precipitate upon further dilution with wash water.



THE EFFECT OF ALCOHOLS ON THE PRECIPITATION OF $(NH_4)_3PO_4.12MoO_3$.

DISCUSSION OF THE EFFECT OF ALCOHOLS

Every alcohol, used in the study, has a disturbing effect on the precipitation of ammonium phosphomolybdate. When large amounts of the various alcohols were present in the samples the results obtained were not in good agreement with each other. There is, however, some similarity between the effects of ethyl, N-propyl, N-butyl, and tertiary butyl alcohols. Yellow precipitates formed when the alcohols were present in small amounts. When larger amounts were used precipitation was prevented and all solutions were colored yellow. When the other two butyl alcohols, secondary and the iso- form, were studied the results indicate that new compounds were, probably, formed.

From the results with ethyl, N-propyl, N-butyl, and tertiary butyl alcohols the degree of disturbance per mol of alcohol shows that probably the length of chain plays a part in the prevention of precipitation of the yellow compound. Since normal yellow precipitates were not found in the presence of secondary and iso-butyl alcohols it is not known if the length of chain in these alcohols plays a part in the prevention of precipitation of the yellow ammonium phosphomolybdate.

FORMIC ACID, HCOOH

Sample No.	Mols added	Mols of $P_2O_5 \times 10^{-6}$ held in solution:
1	0.132	-2.53
2	0.265	-1.41
3	0.265	-4.24
4	0.397	-6.26
5	0.397	-7.18
6	0.529	-8.51
7	0.529	-5.14
8	0.661	-6.62
9	0.794	-0.77
10	0.926	Reaction
11	0.926	Reaction
12	1.058	Reaction

The concentration of P_2O_5 in sample is 48.44×10^{-6}

Beautiful yellow precipitates were thrown down in each sample. When 0.926 mols of formic acid had been added a violent reaction between nitric and formic acids began. The tests were stopped at this point.

ACETIC ACID, CH_3COOH

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.351	-0.49
2	0.435	-0.35
3	0.525	0.42
4	0.612	7.11
5	0.700	48.44
6	0.875	48.44

P_2O_5 in sample is 48.44×10^{-6} mols.

Duplicate runs are not given above. Additional runs have been made, however, and the precipitation of the yellow compound is prevented when 0.700 mols of acid have been added.

The filtrate from sample No. 4 was colored yellow. Instead of giving yellow precipitates, samples Nos. 5 and 6 gave yellow colored solutions. If 1.225 mols of acetic acid are added to a sample, the precipitation of the yellow ammonium phosphomolybdate will be prevented and the solution will take on a yellowish white appearance.

N-PROPIONIC ACID, $CH_3 \cdot CH_2 \cdot COOH$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.133	0.63
2	0.266	0.42
3	0.266	0.91
4	0.399	1.27
5	0.399	1.34
6	0.532	48.44
7	0.532	48.44
8	0.665	48.44

Mols P_2O_5 present in sample equals 48.44×10^{-6}

The first five samples gave colorless solutions and the filtrates were colorless. The remaining three samples gave no precipitates, but the solutions after having been shaken for thirty minutes were colored yellow. The last three samples, shown above, were allowed to stand over night. Small precipitates settled to the bottom of the flasks during the night.

N-BUTYRIC ACID, $CH_3 \cdot (CH_2)_2 \cdot COOH$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.055	-3.16
2	0.109	-2.96
3	0.164	-5.77
4	0.218	0.70
5	0.273	48.44
6	0.327	48.44

Each sample contained 48.44×10^{-6} Mols of P_2O_5

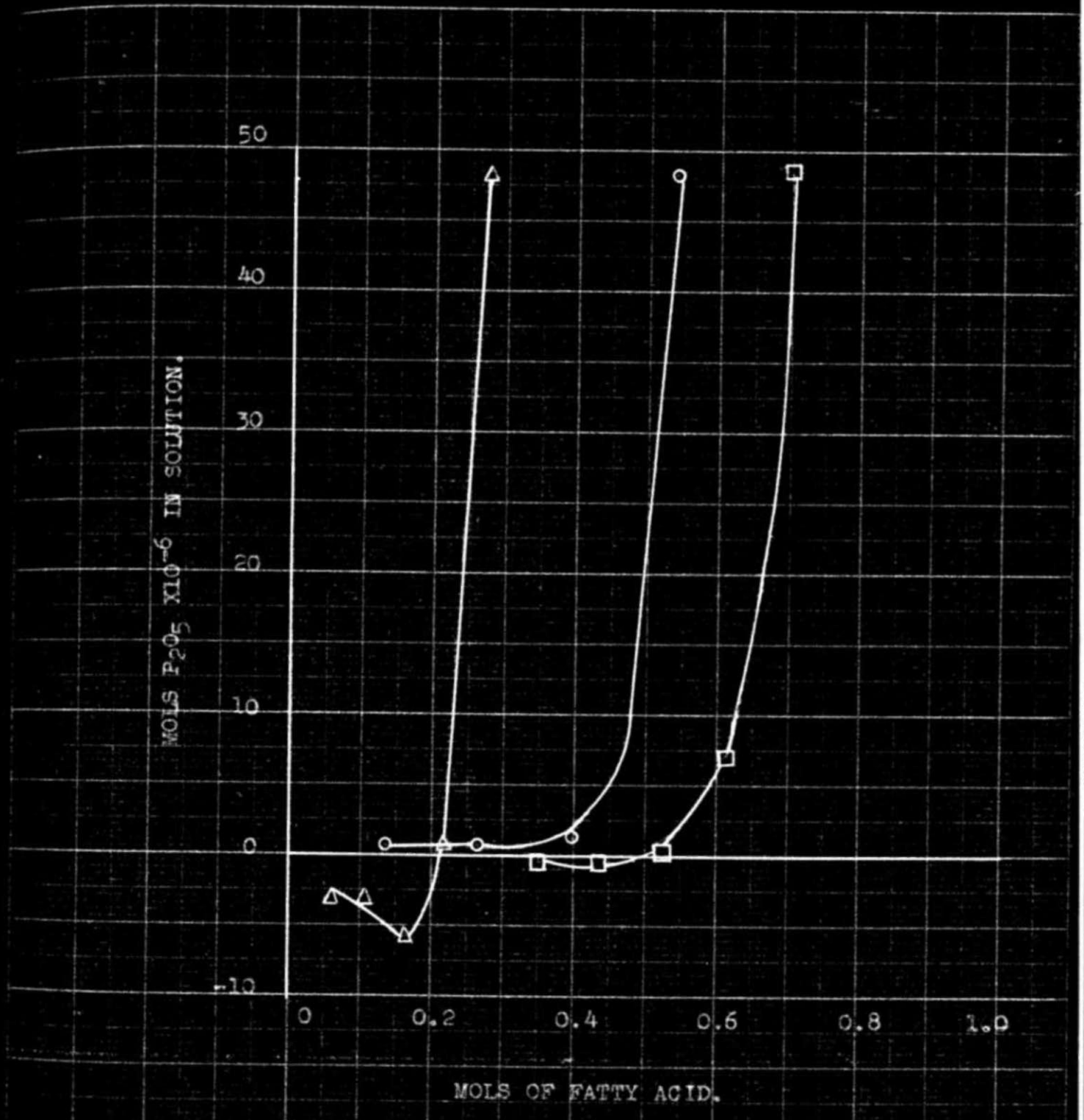
Yellow precipitates were thrown down in the first four samples. The last two samples gave a yellow colored solution but no precipitate. The filtrates resulting from filtration of the first four samples yielded a colorless solution.

ISO-BUTYRIC ACID, $(CH_3)_2CHCOOH$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.054	-3.73
2	0.107	-0.14
3	0.161	-9.85
4	0.215	-2.39
5	0.269	3.38
6	0.322	7.11

P_2O_5 in sample is 48.44×10^{-6} Mols.

Precipitates from the first four samples appeared to be ordinary canary-yellow ones. In the last two samples the solubility of the acid had been exceeded and the precipitates were floating in the acid layer. The water layer was colorless.



THE EFFECT OF FATTY ACIDS ON THE PRECIPITATION OF $(NH_4)_3PO4.12MoO_3$.

DISCUSSION OF THE EFFECT OF THE LOWER MEMBERS OF THE FATTY ACID SERIES

The effects of the straight chain monobasic acids on the reaction are very similar to each other. When precipitation has been prevented by the acids, yellow solutions resulted. (Sufficient tests were not made with formic and iso-butyric acids to determine if complete prevention of precipitation results from the presence of large amounts of these organic acids).

As in the case of the alcohols, the degree of disturbance on the reaction is greater for acids with longer chains.

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OXALIC ACID, $(COOH)_2+2H_2O$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.0015	2.53
2	0.0032	-2.93
3	0.0047	-1.90
4	0.0063	-0.92
5	0.0079	46.89
6	0.0158	46.89
7	0.0238	46.89

P_2O_5 in sample is 46×10^{-6} Mols.

Oxalic acid not only prevents the precipitation of ammonium phosphomolybdate but also destroys the yellow color. Consequently, the qualitative test for phosphorus is destroyed. Samples Nos. 5, 6 and 7 gave neither a yellow precipitate nor a colored solution. If 46.89×10^{-6} mols of P_2O_5 present as the yellow precipitate are added to a small amount of water and heated in the presence of oxalic acid the yellow precipitate will dissolve. The addition of nitric acid, ammonium nitrate, and acid molybdate solution will not re-precipitate the yellow compound.

ETHYLENE GLYCOL, $(CH_2OH)_2$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.180	11.83
2	0.180	11.55
3	0.359	11.75
4	0.359	10.91
5	0.449	9.92
6	0.449	6.20
7	0.540	1.12
8	0.629	3.45
9	0.629	3.17
10	0.719	46.96
11	0.719	46.96

Mols P_2O_5 in sample equals 46.96×10^{-6}

Yellow precipitates were thrown down from all samples except the last two. In these, yellow solutions were formed. The samples giving a yellow precipitate did not give a yellow colored filtrate. Neither did these filtrates give a precipitate nor take on a yellow color on dilution with water. The yellow solutions from samples Nos. 10 and 11 did not give a small yellow precipitate when diluted with wash water.

PYRUVIC ACID, $CH_3COCOOH$

2.5 cc. or 0.036 mols of Pyruvic Acid added to the phosphate solution caused a very small green precipitate to form. The entire solution was colored green. On increasing the concentration of the pyruvic acid in the solution other colors appeared. At 5 cc. concentration of pyruvic acid a black solution but no precipitate formed. A dark straw colored solution resulted from the addition of 10, 12.5, and 15 cc. of acid to the phosphate-molybdate mixture.

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TARTARIC ACID, $HOOC(CHOH)_2COOH$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.0005	1.85
2	0.0005	1.90
3	0.0010	-0.70
4	0.0010	-0.98
5	0.0014	-0.21
6	0.0014	-0.35
7	0.0027	-0.56
8	0.0027	-0.42
9	0.0053	-0.91
10	0.0079	-0.42
11	0.0133	-0.77
12	0.0200	13.44
13	0.0266	48.44
14	0.0333	48.44

The concentration of P_2O_5 in sample is 48.44×10^{-6} Mols.

Samples Nos. 1 to 12 gave a yellow precipitate. The other two samples, Nos. 13 and 14, gave neither a precipitate nor a yellow colored solution. The qualitative test for phosphorus was destroyed when the yellow color failed to develop in samples 13 and 14.

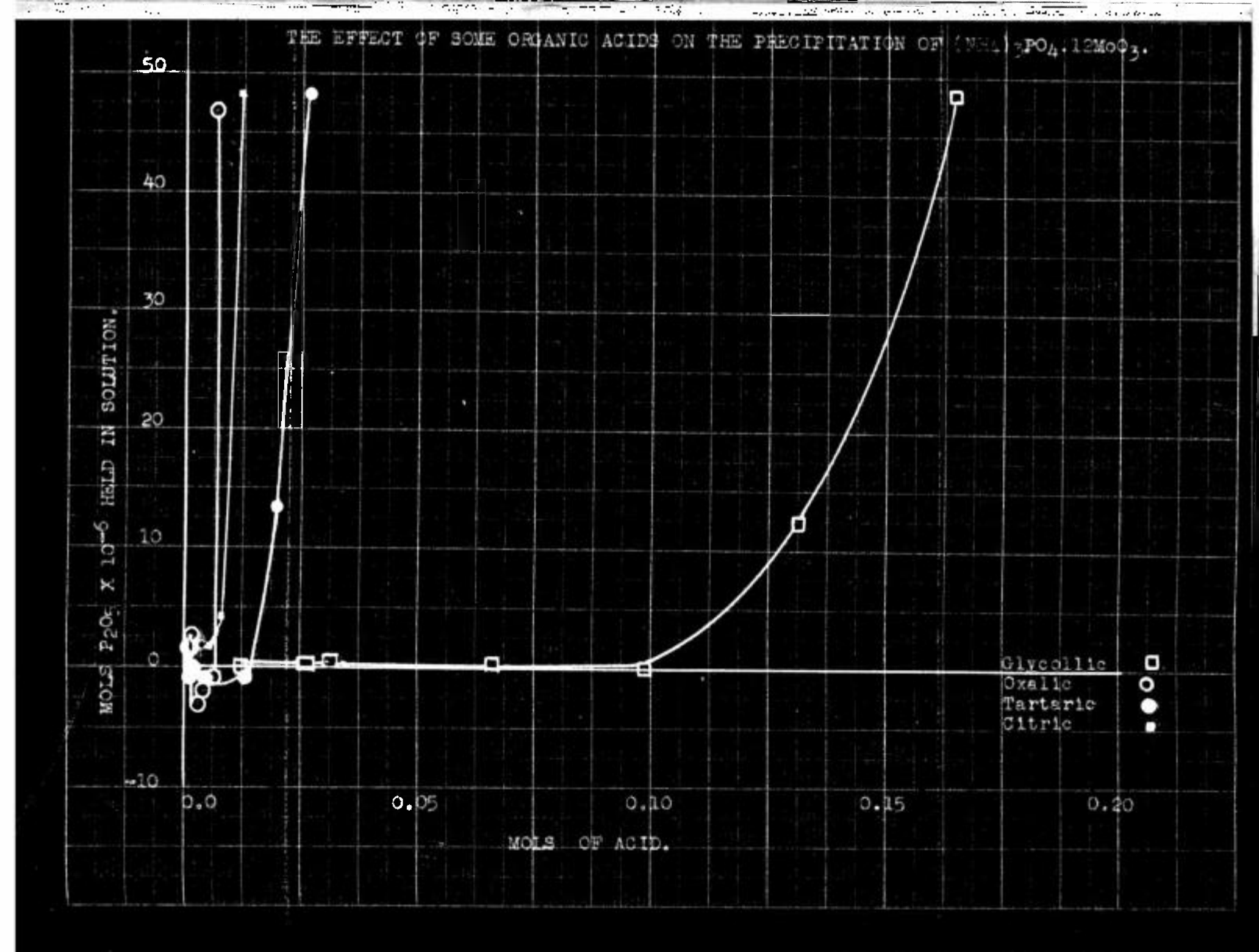
CITRIC ACID, $CH_2COOH \cdot CHOHCCH \cdot CH_2COOH$

Sample No.	Mols added	Mols $P_2C_5 \times 10^{-6}$ held in solution
1	0.0009	1.40
2	0.0009	1.27
3	0.0019	1.34
4	0.0019	1.62
5	0.0038	1.69
6	0.0038	1.97
7	0.0057	1.69
8	0.0057	1.76
9	0.0076	4.15
10	0.0076	4.01
11	0.0095	42.38
12	0.0095	see below
13	0.0114	48.44
14	0.0114	48.44

The concentration of P_2C_5 in sample is 48.44×10^{-6} Mols.

All precipitates formed were canary yellow in color. Samples 11 and 12 gave very small precipitates and samples 13 and 14 gave no precipitates at all. When precipitation of the ammonium phosphomolybdate was completely prevented the solutions remained colorless. The filtrates obtained by filtration of the yellow precipitates were not colored. On dilution with water, the filtrates neither gave a precipitate

nor took on a yellow color. Furthermore, additional ammonium nitrate and nitric acid added to sample No. 12 failed to cause any more precipitation. 10 grams of ammonium nitrate added to sample No. 13 failed to bring down any precipitate. Sample No. 14 was held 24 hours for observation and neither a precipitate nor a yellow color developed during this time.


THE EFFECT OF SOME ORGANIC ACIDS ON THE PRECIPITATION OF (NH4)3PO4.12MoO3.
MOLS P2O5 X 10-6 HELD IN SOLUTION.
50
40
30
20
10
0
-10
0.0
0.05
0.10
0.15
0.20
MOLS OF ACID.
Glycollic
Oxalic
Tartaric
Citric

DISCUSSION OF THE EFFECT OF SOME OTHER ORGANIC ACIDS

The effect of polybasic acids on the precipitation of ammonium phosphomolybdate is more pronounced than that of the fatty acids. Each compound has a different effect on the reaction. It requires less oxalic acid than either tartaric acid or succinic acid to prevent precipitation. Citric acid, which is a tribasic acid, has a great effect on the reaction.

Pyruvic and glycollic acids have disturbing effects on the reaction. The two acids have different effects from each other. Pyruvic acid probably reduces the molybdic oxides into lower valence forms whereas the effect of glycollic acid is very similar to the effect of oxalic, tartaric, and citric acids.

SUCROSE, $C_{12}H_{22}O_{11}$

Sample No:	Grams added:	Mols added:	Mols $P_2O_5 \times 10^{-6}$ held in solution:
1	20	0.058	0.14
2	25	0.073	1.12
3	30	0.088	2.95
4	40	0.117	0.56
5	45	0.132	7.88

Mols of P_2O_5 in each sample equals 48.44×10^{-6}

All precipitates were canary yellow in color. The filtrates, resulting from the removal of precipitates from the solutions, were colorless. Even though all phosphorus had not been precipitated, additional acid molybdate added to the filtrates did not cause any further precipitation of the yellow compound.

ACETONE, $CH_3 \cdot CO \cdot CH_3$

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.034	-0.17
2	0.034	-0.35
3	0.068	-0.70
4	0.068	0.00
5	0.101	0.00
6	0.101	-0.07
7	0.136	-0.07
8	0.204	-0.35
9	0.204	-0.63
10	0.273	11.75
11	0.307	48.44
12	0.307	48.44

Mols P_2O_5 in sample equals 48.44×10^{-6}

The first ten samples gave a yellow precipitate. In addition to a precipitate, sample No. 10 gave a yellow colored solution. Precipitation was prevented in samples 11 and 12 but yellow solutions were present.

If precipitation is carried out in the presence of four grams instead of the usual eight grams of ammonium nitrate 0.273 mols of acetone will prevent the precipitation of ammonium phosphomolybdate.

Another run was made containing a slightly weaker solution of phosphate. Entirely new solutions were

used but the same method of procedure was employed in this run that was used in the one given above. The results are:

Sample No.	Mols added	Mols $P_2O_5 \times 10^{-6}$ held in solution
1	0.136	-0.56
2	0.136	-0.07
3	0.204	-0.49
4	0.204	-0.28
5	0.273	2.96
6	0.273	3.03
7	0.307	46.89
8		
8	0.307	46.89

The concentration of P_2O_5 in sample equals 46.89×10^{-6} Mols.

Beginning with sample No. 5 and continuing through No. 8, the solutions were colored yellow. Nos. 7 and 8 gave no precipitates. With the exception of those samples containing 0.273 mols of acetone, the results of the two runs are in excellent agreement.

Still another run with acetone was made to study the effect of increasing the concentration of ammonium nitrate in the sample when sufficient acetone was present to prevent the formation of a yellow precipitate when only 8 grams of nitrate were used. 0.341 mols of acetone was added to several flasks, along with the usual amount of phosphate solution and acid molybdate.

The total volume of the sample was held constant at 150 cc. Ammonium nitrate was added in varying amounts from eight to sixteen grams. After shaking the samples for thirty minutes, the only precipitates formed were in those samples containing sixteen grams of nitrate. The precipitates formed were very small sticky ones and all solutions were colored yellow. It is doubtful if the yellow precipitate formed, by the addition of sixteen grams of nitrate, is an ordinary precipitate of ammonium phosphomolybdate. At least, the precipitate is very sticky and does not have the appearance of ammonium phosphomolybdate.

DISCUSSION OF RESULTS

The effect of organic matter on the precipitation of ammonium phosphomolybdate is complicated. All organic compounds seem not to have the same characteristic effect. For example, there are certain compounds, such as oxalic and tartaric acids, that prevent the formation of the yellow precipitate and at the same time give a colorless solution. There are other compounds, such as ethyl alcohol and acetic acid, which prevent the formation of the yellow precipitate and give a yellow solution.

Some organic substances not only prevent the precipitation but seem to have a solvent effect. For example, tartaric acid when present in very small amounts probably dissolves part of the precipitate. Yet, when larger amounts are present the solvent effect is probably counterbalanced by a disturbing effect on the reaction. Thus, a precipitate is thrown down which requires more sodium hydroxide to dissolve it than the precipitate would have required if no organic matter had been present during the precipitation.

Another thing inexplicable at this time is the sudden effect or instantaneous prevention of formation of the yellow precipitate when the organic matter has been increased by only a small amount.

A nice yellow precipitate will form when a certain concentration of organic matter is present. Yet, the

organic matter may be increased, usually by less than 0.1 mols per sample, and precipitation is completely prevented.

The results of this investigation bear out the statement of Hundeshagen that organic matter interferes with the formation of ammonium phosphomolybdate. Every organic compound studied has some effect on the reaction.

Contrary to the statement of Maderna, it has not been found practical to add sufficient nitric acid to cause the precipitation of all phosphorus when large amounts of organic matter are present. The concentration of nitric acid will have to be so large that any yellow precipitate will dissolve immediately in the strong acid. A small precipitate will form when a small amount of nitric acid is added to a sample where precipitation has been prevented by certain organic compounds, such as acetone, ethyl alcohol, and acetic acid. Additional nitric acid will not cause a precipitate to form when such substances as tartaric or citric acids are present. In no case has it been feasible to add sufficient nitric acid to cause complete precipitation when large amounts of organic matter are present.

In addition to the information found concerning the disturbing effect of organic matter on the precipitation of ammonium phosphomolybdate, we have learned many other things of interest.

The "official method," used by most agricultural

laboratories for the determination of phosphorus in soils, fertilizers, etc., states that any mineral acid, in the presence of phenolphthalein as an indicator, can be used for titrating the excess sodium hydroxide, after ammonium phosphomolybdate has been dissolved in the excess base. We have found that sulphuric acid can not be used satisfactorily for accurate titration when phenolphthalein is used as an indicator. A milky color appears near the end-point and an accurate titration with this acid is almost impossible. In fact, sulphuric acid causes a milky color to appear in any ordinary titration of sodium hydroxide when phenolphthalein is used for the indicator. In the phosphate titration, nitric acid gives the clearest endpoint and hydrochloric gives a satisfactory sharp endpoint. Hydrochloric acid is more suitable to use since nitric acid will not remain standardized for any considerable length of time.

When the Pemberton Method is used for the estimation of phosphorus in ammonium phosphomolybdate, ammonium nitrate solution should not be used to wash the precipitate. A good many quantitative texts, such as Scott's "Methods of Chemical Analysis," suggest either ammonium or potassium nitrate solutions for the wash. Lundell and Hoffman (8) only use 1% solution of potassium nitrate to remove the nitric acid from the precipitate. We have found that all ammonium phosphomolybd-

ate precipitates when washed with ammonium nitrate and dissolved in a base can not be estimated accurately by titration. On addition of acid to titrate the excess base in the solution, the pink color gradually fades until the liquid is colorless. By adding a few drops of phenolphthalein a faint pink color will reappear. This peculiar phenomenon will occur until the pink color has been destroyed about four to five times. In the case when potassium nitrate solution has been used for the wash the endpoint is clear and any additional phenolphthalein added will not cause the pink color to reappear.

CONCLUSION

It is evident, from the data given in this paper, that organic substances have a disturbing effect on the precipitation of ammonium phosphomolybdate. The disturbing effect seems to be different with different organic compounds. Nitric acid will not prevent the effect even though large amounts may be added to the solution containing the mixture of phosphate-molybdate solution.

The nature of the true effect of organic matter on the reaction is unknown. However, it is believed that the right road leading to the solution of this problem can be found by determining the cause of a precipitate formation which requires more sodium hydroxide to dissolve it than would be required if the precipitate had been formed in the absence of organic matter.

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